Summary

Acid gases are frequently present in industrial gases and have to be removed for corrosion prevention, operational, economical and/or environmental reasons respectively. A vast amount of commercial processes are available to deal with the acid gas removal. Chemical absorption using an aqueous alkanolamine solvent is the most commonly used process in the gas treating industry. In this process the acid gas is contacted with a solvent in an absorber and, via chemical reactions, converted to non-volatile species in the liquid. The acid gas containing solvent is routed to a desorber, where the acid gas is released from the solvent at a higher temperature and/or lower pressure. For the design of gas treating equipment a reliable rate based simulation program is required, which describes the involved complex mass transfer phenomena accurately. The thermodynamics of the acid gas – solvent system play also a very important role in the mass transfer model. To describe these thermodynamics an accurate thermodynamic model is required, which has to be validated with experimental data.

In this thesis a new thermodynamic model for acid gas – alkanolamine systems has been used and further developed. This model, based on an electrolyte equation of state (E-EOS) was originally introduced by Fürst and Renon (Fürst, W.; Renon, H. Representation of excess properties of electrolyte solutions using a new equation of

state, *AIChE Journa*l, 39 (1993) 335-343). In this electrolyte equation of state approach both the vapor and the liquid are described with an equation of state. Several ionic terms needed to be added to this equation of state approach in order to take into account the additional interactions due to the ions present in the liquid. In this thesis the E-EOS model has been developed to study the solubility of the acid gases carbondioxde (CO_2) and hydrogensulphide (H_2S) in aqueous N-Methyldiethanolamine (MDEA) respectively. MDEA is commonly used in the gas treating industry for selective H_2S removal, but it is also used for other applications. Initially, the E-EOS has been used to study the acid gas solubility at low total system (atmospheric) pressures. These solubility data are available widely in the literature. However, the pressure in an absorber of a natural gas plant is in general significantly higher. Therefore, also new acid gas (CO_2 and/or H_2S) solubility data in aqueous MDEA were determined at high partial pressure of methane (up to 69 bar). These experimental solubility data are compared also with the E-EOS model developed in this study.

In Chapter 2 an overview of several thermodynamic models is presented, which can be used to describe the thermodynamics of an acid gas – alkanolamine system. Each thermodynamic model/approach has its own specific pro and cons. At high pressure applications (i.e. natural gas), however, an electrolyte equation of state seems to be very attractive, due to the uniform approach of both the liquid and the vapor phase respectively.

In Chapter 3 the electrolyte equation of state as developed by Solbraa (Solbraa, E, *Ph.D. Thesis Norwegian University of Science and Technology* (2002)) was further developed to study the solubility of CO_2 in aqueous MDEA. The improved model has been compared with solubility data for the system CO_2-H_2O-MDEA as presented in the open literature. The calculated (speciated) liquid composition is compared with speciation data (with a NMR technique) as presented in the literature. The prediction of the speciation with the E-EOS appeared to be very well

in line with the NMR data. In Appendix A new CO_2 solubility data in aqueous MDEA are presented at different liquid loadings (0.047 – 1.105 mol.mol^{-1}), temperatures (283 and 298 K), MDEA concentrations (35 and 50 wt.%) and partial pressures of methane (up to 69 bar). It has been demonstrated (experimentally and by E-EOS) that both the system pressure and/or partial pressure of methane have a significant effect on the solubility of CO_2 in aqueous MDEA solutions respectively. A decrease in CO_2 solubility has been observed, when the partial pressure of methane is increased. It is concluded from E-EOS simulations that this decreasing solubility is caused by a lowering of the CO_2 fugacity coefficient at increasing methane partial pressure.

In Chapter 4 the electrolyte equation of state as described in Chapter 3 is further extended to calculate the solubility of H_2S in aqueous MDEA. Several, H_2S specific pure component and binary interaction parameters have been included in the E-EOS. The model has been validated with solubility data of H_2S in aqueous MDEA in the absence and the presence of methane as a make-up gas respectively. In Appendix A new H_2S solubility data in aqueous MDEA are presented at different liquid loadings (0.028 – 0.075 mol.mol^{-1}), temperatures (283 and 298 K), MDEA concentration (35 and 50 wt.%) and partial pressures of methane (up to 69 bar). For both the system H_2S-MDEA-H_2O and H_2S-MDEA-H_2O-CH_4 the model under-predicts the acid gas partial pressure (and over-predicts the acid gas solubility). However, model predictions for the system in absence of methane are much more in agreement with the experimental data. Both experimental data and model calculations show that an increase in partial pressure of methane results in a decrease of H_2S solubility. It is concluded from E-EOS simulations that this decreasing solubility is caused by a decreasing H_2S fugacity coefficient at increasing methane partial pressure.

In Chapter 5 the solubilities of CO_2 and H_2S, when present simultaneously in aqueous MDEA, have been studied experimentally and theoretically. This is with

and without methane acting as inert component. New datapoints are presented for 35 and 50 wt.% aqueous MDEA at 283 and 298 K and several liquid loadings. The methane partial pressure has been varied from 6.9 up to 69 bar. The H_2S partial pressure increases significantly with the CO_2 liquid loading, i.e. the capacity of the solvent for H_2S capture decreases. The experimental results are compared to the electrolyte equation of state as developed for single gas systems in Chapter 3 and 4 of this thesis. When CO_2 and H_2S are present simultaneously, only one additional new parameter is required compared with the two single gas E-EOS modules. Only the value of the CO_2-H_2S molecular interaction parameter needs to be determined. During simulations with the E-EOS it appeared that the model results were hardly sensitive to the value of this parameter. Initially, the E-EOS was compared with solubility data in open literature for the system CO_2-H_2S-MDEA-H_2O. In general it can be concluded that the E-EOS is able to predict the simultaneously solubility of CO_2 and H_2S in aqueous MDEA satisfactorily. The E-EOS model is also compared to the experimental data of the CO_2-H_2S-MDEA-H_2O-CH_4 system as presented in Chapter 5. The model is also able to predict these experimental results with good agreement.

Based on the results as described in this thesis, it is concluded that the electrolyte equation of state (E-EOS) approach gives very promising results for the prediction of the thermodynamics of acid gas – alkanolamine systems. It has been proven that the model can be extended from binary non-reactive systems, to reactive single gas systems (CO_2 and H_2S) and to reactive systems, where these acid gases are present simultaneously. It is expected that the model can be improved significantly, when more experimental physical and chemical equilibrium data are available. For example the following data are scarce in the (gas treating) literature:

- *Binary thermodynamic data*
  VLE, heat of mixing, etc of binary water – alkanolamine systems;

- *Speciation data of the reactive acid gas – alkanolamine system*
  At the moment the several ionic interaction parameters are determined from total acid gas solubility data. However, these parameters can be determined more accurately, when the concentration of the several molecular and ionic species in the liquid is known. When these speciation data are available, the molecular CO_2 concentration does not have to be estimated from the CO_2-N_2O analogy as done in this thesis, but can be determined directly;
- *Thermodynamic data at high (methane partial) pressure*
  In general the thermodynamic data are determined during low (atmospheric) pressure. However, in this thesis it has been proven that the (methane partial) pressure plays an important role on the acid gas solubility. Substantially more research is also required in this area to study the influence of other inert components, such as nitrogen, oxygen and other hydrocarbons on the acid gas solubility in aqueous alkanolamine solutions.